

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 5 :</b> <b>C08F 299/00</b>		<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/07930</b> <b>(43) International Publication Date:</b> <b>14 April 1994 (14.04.94)</b>
<b>(21) International Application Number:</b> <b>PCT/US93/08833</b>			<b>(74) Agents:</b> BUTTS, Evan, K. et al.; Exxon Chemical Company, P.O. Box 5200, Baytown, TX 77522 (US).
<b>(22) International Filing Date:</b> <b>17 September 1993 (17.09.93)</b>			<b>(81) Designated States:</b> AU, CA, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
<b>(30) Priority data:</b> <b>07/954,539</b>	<b>29 September 1992 (29.09.92)</b>	<b>US</b>	<b>Published</b> <i>With international search report.</i>
<b>(71) Applicant:</b> EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US).			
<b>(72) Inventors:</b> BRANT, Patrick ; 103 Harborcrest, Seabrook, TX 77586 (US). CANICH, Jo, Ann, Marie ; 900 Henderson Avenue, Apt. 808, Houston, TX 77058 (US). DIAS, Anthony, Jay ; 1411 Quite Green Court, Houston, TX 77062 (US). BAMBERGER, Robert, Lee ; 15903 Sea Palms, Crosby, TX 77532 (US). LICCIARDI, Gary, Frederick ; 20003 Big Timber, Humble, TX 77346 (US). HENRICHES, Paul, Mark ; 2209 Maconda, Houston, TX 77027 (US).			
<b>(54) Title:</b> LONG CHAIN BRANCHED POLYMERS AND A PROCESS TO MAKE LONG CHAIN BRANCHED POLYMERS			
<b>(57) Abstract</b>  A novel polymer and process for producing polymers incorporating linear long chain side branches are provided. The long chain linear branches occur at a frequency of less than 5.0 branches per 1000 carbon atom of the main polymer chains with at least some branches having a molecular weight greater than the critical molecular weight for entanglement of the polymer. The linear long chain branched polymers are produced by alpha-olefin macromolecule incorporation during bridged metallocene catalyst polymerization in solution and slurry processes. The polymers are characterized by superior processability characteristics of the polymer melts and superior mechanical characteristics of the solid polymers. The polymers are useful for fabrication into a wide variety of articles by conventional fabrication techniques.			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	PR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	CN	Guinea	NL	Netherlands
BP	Burkina Faso	GR	Greece	NO	Norway
BC	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TC	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

TITLE5                   LONG CHAIN BRANCHED POLYMERS AND A PROCESS TO MAKE LONG  
                  CHAIN BRANCHED POLYMERSFIELD OF THE INVENTION10                  This invention relates to the field of long chain  
                  branched polymers and a process to make them.BACKGROUND OF THE INVENTION15                  This invention relates to novel polyolefin  
                  polymers, processes for producing such polymers, and  
                  applications for such polymers. The commercial  
                  significance of polyolefin polymers is enhanced by the  
                  variety of forms they may take which often exhibit  
                  different physical properties. These different  
                  properties make polyolefin polymers useful in many  
20                  different end use applications. The structural  
                  features of polyolefins that are considered most  
                  significant are molecular weight, which is related to  
                  polymer chain length, the type and tacticity of side-  
                  chain branches, and the distribution of side-chain  
25                  branches along the main polymer chains. Over the  
                  years, considerable attention has been given to the  
                  molecular architecture of polyolefins. Polyolefins can  
                  be commercially produced using any one of a number of  
                  processes. The random nature of most polymerization  
30                  processes results in a heterogeneous polymer, rather  
                  than a truly homogeneous polymer product. Polyolefins  
                  produced by classical Ziegler-Natta catalysts consist  
                  of mixtures of molecules of different molecular weights  
                  and different amounts of comonomer incorporation.  
35                  These differences result from the differences in  
                  catalysts used, and differing rates of comonomer  
                  incorporations. Other factors influencing polymer

products include choice of monomers, catalyst reactivity or ability to incorporate comonomers, and differing polymerization process conditions.

Commercial polyethylenes fall into one of two general categories, linear polyethylenes (LPEs) and "conventional" low density polyethylenes (LDPEs). LPEs are traditionally produced by addition polymerization of ethylene, or by the copolymerization of ethylene and an alpha-olefin comonomer, in a variety of processes using coordination catalysts. LDPEs are traditionally produced by free-radical polymerization of ethylene in high temperature and high pressure reactors using peroxide initiators. These two broad categories of polyethylenes have significant structural and physical differences. The most important difference between LPEs and LDPEs is the nature of the side-chain branching. LDPEs are highly side-chain branched having dendritic (tree-like) long chain side branches attached to the main polymer chains. These branches are created as a result of inter-molecular chain transfer during free-radical polymerization. Dendritic side-chain branching gives certain advantages, particularly processing advantages, to the polymer melts. However these processing advantages are balanced by disadvantages inherent with LDPEs relating to mechanical properties of the solid polymers such as lower stiffness, hardness, low tear resistance, low environmental stress crack resistance (ESCR) and, low tensile strength. These properties relative to LPEs with equivalent density and melt index properties.

Likewise, LPEs without long chain side branches have good mechanical properties such as good stiffness, hardness, tensile strength characteristics, tear resistance, and ESCR; however, from a processing standpoint, LPEs have the disadvantages of a tendency to melt fracture and low shear sensitivity resulting in

high melt viscosity, low melt strength and higher processing costs.

Polyethylene producers have spent considerable time and resources over the years trying to produce polymers possessing the polymer melt processing advantages of LDPEs and the mechanical properties advantages of solid LPEs. Most efforts have centered around adding long branches to LPEs. One conventional method of producing long chain branches in LPEs is to copolymerize ethylene with alpha-omega dienes. This method is illustrated in U.S. Patent 3,984,610, PCT application 91-17,194 and Japanese KOKAI 02-261,809, which are incorporated by reference herein.

In this method, dienes are simultaneously incorporated into propagating chains, thereby creating a covalent bridge between two linear molecules. The resulting structure in the vicinity of the bridge is typically shaped like the letter "H". The resultant side-chain branches can be long and are usually paired rather than isolated. As the number of dienes per molecule increases, the complexity of the branching approaches that of dendritic branching ultimately causing the polymer to lose its linear mechanical characteristics. In addition to mechanical properties shortcomings, polymers produced with dienes have encountered resistance to approval by regulatory authorities for food contact applications.

Other methods to produce long chain branches on LPEs involve post-polymerization treatments of linear molecules. Several different types of post-polymerization treatments have been used. United Kingdom Patent 901,148 demonstrates the production of branched polyethylene by treating molten polyethylene with oxygen. One method of doing this is by forcing air into the molten polyethylene during melt extrusion. This method of production results in non-linear long chain branches. United States Patent 4,586,995,

discloses the irradiation of molten polyethylene in the absence of oxygen to produce Y branches having two to fifty carbon chains per ten thousand carbon atoms in the main polymer chain. United Kingdom Patent 5 1,379,853 discloses the introduction of branches into polyethylene during the degradation of high density polyethylene in the presence of an organic peroxide. This process will result in dendritic side branches. Finally, Japanese Kokai 59-59,760 discusses the 10 production of long chain branched polyethylene by heating polyethylene containing a terminal vinyl group at 180° - 360°C under vacuum conditions or an inert atmosphere for five minutes to six hours. The polymer produced has long chain branches with a frequency of 15 3.5 branches per molecule. These branches are non-linear.

A third type of process for producing branching in linear polyethylene is the use of a polymerization cocatalyst which contains a long chain branched 20 polymeric group. U.S. Patent 4,500,648 and divisionals thereof disclose high density polyethylene production with branches prepared by polymerization of ethylene in the presence of a coordination catalyst containing an organoaluminum compound having a branched polymeric 25 hydrocarbyl group as one of its substituents. The polymers produced by this method contain non-linear long chain branches.

A method for the preparation of LLDPE using only ethylene is described in European Application Number 30 87108556.9 EPA 250,999. The method used is the oligomerization of ethylene using nickel based catalysts followed by copolymerization of the olefin mixture with ethylene through use of a chromium catalyst system. The objective of this application is 35 to utilize a process for preparing higher olefins to prepare a mixture of olefins which is then copolymerized to yield the LLDPE structure. The LLDPE

prepared in this method consists of polyethylene with a distribution of side-chains having 14 to 200 carbon atoms. One deficiency of this application is that it utilizes very low activity catalysts to form the 5 oligomers and the subsequent copolymers. Secondly, this application does not recognize the importance of utilizing even longer side-chains than those described in the application.

A method for producing LLDPE containing long-chain 10 branches is described in European patent application 91301811.5 EPA 446,013 and Japanese application H1- 251748. EP 91301811.5 presents the polymerization of ethylene using Nickel complexes to give LLDPE containing long-chain branching. JP H1-251748 presents 15 the copolymerization of ethylene and hexene using Nickel based polymerization catalysts. Using the catalyst systems described in the application, ethylene copolymers containing short and long chain branches are produced. The chief limitations of these applications 20 are those known for Nickel based catalyst systems: 1) the low catalyst activities (30 g polymer/mmol catalyst in 1 hr); and 2) molecular weight distribution is proportional to molecular weight, therefore high molecular weights are accompanied by broad molecular 25 weight distributions. This method does not produce higher Mw with narrow Mw/Mn.

#### SUMMARY OF THE INVENTION

This invention relates to novel polymers and 30 processes for making polymers incorporating linear long chain side branches. The term "linear" is herein defined to include side chains that have some side chain branching but are not dendritic. The linear long chain branches are comprised of sidechains being at 35 least 250 carbons long, which have molecular weights at least as great as the critical molecular weight for entanglement ( $M_c$ ) of the polymer. The linear long

chain branches occur at a frequency of less than 5.0 branches per 1000 carbon atoms in the main polymer chains. The linear long chain branched polymers are produced by incorporating a macromolecule during 5 metallocene-catalyzed solution polymerization processes (solvent or bulk process at low, medium or high pressure). The long chain branched polymers possess the processability characteristics of conventional long chain branched polymer melts and the mechanical 10 characteristics of conventional solid linear polymers. Polymers produced in accordance with this invention are useful for fabrication into a wide variety of articles by injection molding, extrusion coating and molding, blown film, cast film, thermoforming and rotational 15 molding.

#### DETAILED DESCRIPTION OF THE INVENTION

During traditional coordination-catalyst polymerization of polyethylenes, most polymer chains 20 are terminated by the beta-abstraction mechanism which results in terminal unsaturation. If the molecule terminates after incorporation of a comonomer, the result is vinylene or vinylidene unsaturation. If the molecule terminates after the incorporation of 25 ethylene, the result is vinyl unsaturation. A vinyl unsaturated molecule can be considered a large alpha-olefin.

Linear copolymers are produced by additional polymerization of two or more vinyl terminated monomers 30 ranging in size from two to thirty carbon atoms. In the present invention, copolymers are produced in which vinyl terminated polymers, also called macromonomers or macromers, are incorporated into the addition polymerization reaction along with the monomers. The 35 vinyl terminated polymers responsible for the unique characteristics of polymers produced in accordance with the present invention are molecules having molecular

weights greater than the critical molecular weight for entanglement ( $M_C$ ) of the polymer into which the vinyl terminated polymers are incorporated. The  $M_C$  for polyethylene is 3,800. The vinyl terminated polymers of this invention are 250 or more carbon atoms long, preferably 350 to 3500, even more preferably 300 to 3000, or have a  $M_w$  of greater than 6000. Further, the vinyl terminated polymers of this invention are incorporated into the growing polymer at an average frequency of no more than 5 long side chains per 1000 carbon atoms along the main chain, preferably the average frequency is 0.2 to 3 long side chains per 1000 carbon atoms, more preferably 0.9 to 2 long side chains per carbon atoms.

Using traditional coordination catalyst processes, these vinyl terminated polymers do not incorporate into growing polymer chains. The inventors have discovered that using certain metallocene catalysts, preferably under solution process conditions, in accordance with the present invention will result in these vinyl terminated polymers being incorporated into growing polymer chains at controllable amounts of incorporation. As these vinyl terminated polymers are incorporated into propagating polymer chains, they become isolated long chain branches of that polymer chain. The inventors have found that long chain branches, in accordance with the present invention, yield polymers having the positive mechanical attributes of solid linear polyolefins, while having the positive processing characteristics of melts of branched polyolefins.

The vinyl terminated polymers of this invention which eventually become side chains can be homopolymers or copolymers of one or more  $C_2$  to  $C_{30}$  olefin, preferably alpha olefins, even more preferably homo or copolymers of ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methylpentene-1. Cyclic

olefins are also useful monomers in the practice of this invention. Likewise, the main chain can also be a homopolymer or copolymer of one or more C<sub>2</sub> to C<sub>30</sub> olefins, preferably alpha olefins, even more preferably 5 homo or copolymers of ethylene, propylene, butene-1, pentene-1, hexene-1, octene-1 and 4-methyl-pentene-1. Copolymer is herein defined to include polymers of 2 to 4 different monomers and block copolymers of any of the above olefins or alpha olefins.

10 The vinyl terminated polymers useful in this invention can be prepared using a variety of metallocene catalysts and process conditions. The particular choice of catalyst and process conditions depends upon the desired polymer composition and 15 molecular weights. High vinyl termination content is necessarily preferred. Preferably about 0.9 to about 1.1 chain end unsaturations per macromer are present, even more preferably about 1 chain end unsaturation per macromer. Conditions which favor their formation are 20 high temperatures, no comonomer, no transfer agents like hydrogen, and a non-solution process or a dispersion using an alkane diluent. Thus the metallocene should be active at relatively high temperatures. The selected metallocene may also be 25 thermally activated to yield the beta-hydrogen eliminated product; vinyl ends. Thus one could prepare materials at low temperature then increase the temperature to get the beta-hydride eliminated product. The steric requirements of the metallocene will affect 30 the degree to which copolymerization occurs. Metallocenes which possess steric hindrance will yield vinyl terminated polymers which are relatively free of branches when compared to metallocenes which do not possess this hindrance.

35 Another method producing vinyl termination involves production of polymer with an ethylene "cap" or end with the needed vinyl group. This could be

accomplished by beginning polymerization at a low temperature, for example, below zero degrees Celsius, and raising the reaction temperature at the "end" of the reaction, for example, to above ten degrees

5 Celsius, and simultaneously adding ethylene so that the ethylene preferentially polymerizes to form an end "cap" or block. A block copolymer of ethylene and a C<sub>3</sub> to C<sub>30</sub> alpha olefin would also present the necessary vinyl termination.

10 The vinyl terminated polymers can be optimally copolymerized using metallocenes which are sterically unhindered. In addition the polymerization system should be a single-phase, or if two-phase, the vinyl terminated polymers must be sufficiently mobile to 15 permit their copolymerization. The preferred process for their copolymerization is a solution process. Thus the process solvent and temperature preferred are those in which the vinyl terminated polymer is soluble or substantially swollen.

20 The present invention preferably utilizes catalyst system comprising a metallocene catalyst with cocatalyst activators of an alumoxane or a "non-coordinating" anion. The metallocene catalyst is an activated cyclopentadienyl group 4 transition metal compound. In particular, the metallocene catalysts employed in this invention are organometallic coordination compounds which are cyclopentadienyl derivatives of group 4 metals of the periodic table of the elements and include mono-, di- and tri- 25 cyclopentadienyls and their derivatives. Particularly desirable are the metallocenes of the group 4 metals: titanium, zirconium and hafnium. The cyclopentadienyl metallocenes of this invention can be activated with either an alumoxane or a "non-coordinating" anion-type activator. In general at least one metallocene 30 compound is employed in formation of the catalyst system. Metallocenes employed in accordance with this 35

invention contain at least one cyclopentadienyl ring and preferably comprise titanium, zirconium, or hafnium, most preferably hafnium, or zirconium for bis-cyclopentadienyl compounds and titanium for mono-cyclopentadienyl compounds. The cyclopentadienyl ring can be substituted or unsubstituted or contain one or more substituents e.g. from 1 to 5 substituents such as for example, hydrocarbyl substituent e.g. up to five C<sub>1</sub> to C<sub>20</sub> hydrocarbyl substituents or other substituents e.g. for example, a trialkyl cyclic substituent. A metallocene may contain 1, 2 or 3 cyclopentadienyl rings, however, two rings are preferred for use with hafnium or zirconium. One ring is preferred for use with titanium.

15 The catalyst system used in this invention can be described as comprising cyclopentadienyl transition metal catalyst having at least one delocalized pi-bonded moiety and an activating cocatalyst. The catalyst system used in this invention can also be described as comprising a cyclopentadienyl transition metal catalyst of a transition metal compound containing a single cyclopentadienyl group and a heteroatom containing group each bonded to the transition metal, said cyclopentadienyl group and heteroatom containing groups optionally bridged through a divalent moiety and an activating cocatalyst.

20 In another embodiment of the present invention the macromonomer can be polymerized in a gas phase process. This may be achieved by pre-polymerizing the macromonomer by one of many methods known in the art. For example, the method for supporting a catalyst known in U.S. Patent Application 885,170 filed 5-18-92, incorporated by reference, discloses how to place a catalyst on a support. This supported catalyst can 25 then be combined with the macromonomer under appropriate polymerization conditions to pre-polymerize the macromonomer with the supported catalyst. This

combination can then be introduced into a gas phase polymerization reactor to produce long chain branched polymers in this invention.

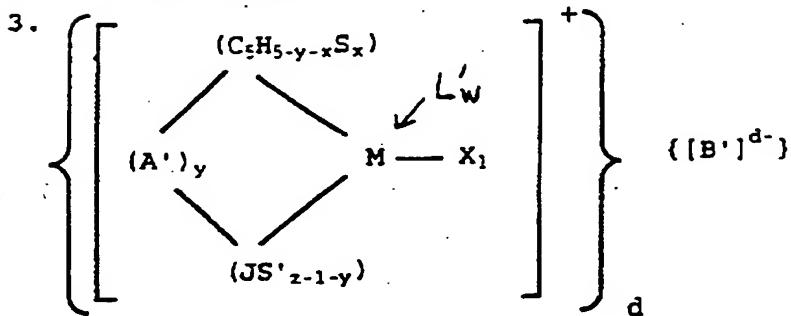
This macromonomer may also be pre-polymerized with  
5 other traditional gas phase supported catalysts and  
similarly introduced into the gas phase polymerization  
reactor. Likewise, one could use a two step process  
wherein the macromonomer or the catalyst is first  
placed on support using techniques known in the art and  
10 then the catalyst and/or the macromonomer are added later  
to form the supported pre-polymerized catalyst  
combination. As is well known in the art, the pre-  
polymerization process is normally a slow, controlled  
15 process to initiate controlled polymer fracture or  
support fracture thus, one of ordinary skill in the art  
would be sure to maintain appropriate reaction  
conditions such as temperatures from 40°C to 140°C in a  
suitable solvent with the introduction of ethylene, or  
20 suitable comonomers to form the macromonomers in a  
controlled amount.

#### Ionic Catalyst System - General Description

The process of this invention is practiced with  
that class of ionic catalysts referred to, disclosed,  
25 and described in European Patent Applications EP 0 277  
003 A1 and EP 0 277 004 A1, and PCT Application WO  
92/00333, and U.S. Patents 5,055,438 and 5,096,867,  
which are herein incorporated by reference. The ionic  
catalysts used in this invention can be represented by  
30 one of the following general formulae (all references  
to groups being the new group notation of the Periodic  
Table of the Elements as described by Chemical and  
Engineering News, 63(5), 27, 1985):

12

1.  $\{[(A-Cp)MX_1]^+d\} \{[B']^{d-}\}$   
 2.  $\{[(A-Cp)MX_1L]^+d\} \{[B']^{d-}\}$



wherein:

(A-Cp) is either (Cp) (Cp\*) or Cp-A'-Cp\*; Cp and Cp\* are the same or different cyclopentadienyl rings  
 15 substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-  
 20 substituted organometalloid, disubstituted boron, disubstituted Group 15 element, substituted Group 16 element or halogen radicals, or Cp and Cp\* are  
 25 cyclopentadienyl rings in which any two adjacent S groups are joined forming a C4 to C20 ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

A' is a bridging group, which group may serve to restrict rotation of the Cp and Cp\* rings or (C5H5-y-xSx) and JS'(z-1-y) groups;

30 (C5H5-y-xSx) is a cyclopentadienyl ring substituted with from zero to five S radicals;

x is from 1 to 5 denoting the degree of substitution;

M is titanium, zirconium, or hafnium;

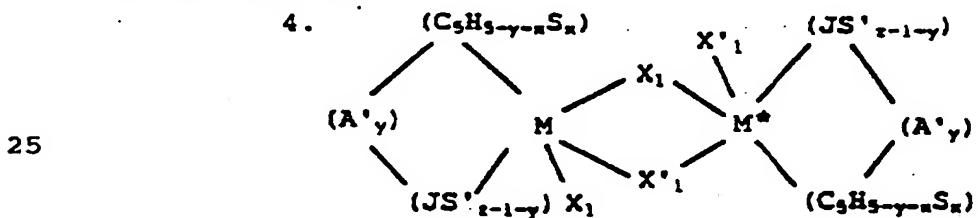
35 X1 is a hydride radical, hydrocarbyl radical, substituted-hydrocarbyl radical, hydrocarbyl-substituted organometalloid radical or halocarbyl-

substituted organometalloid radical which radical may optionally be covalently bonded to both or either M and L or all or any M, S, or S';

(JS<sub>z-1-y</sub>) is a heteroatom ligand in which J is an element from Group 15 of the Periodic Table of Elements with a coordination number of 3 or an element from Group 16 with a coordination number of 2; S is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-substituted organometalloid; and z is the coordination number of the element J;

y is 0 or 1;

15 L is an olefin, diolefin or aryne ligand, or a neutral Lewis base; L' can also be a second transition metal compound of the same type such that the two metal center M and M\* are bridged by  $X_1$  and  $X'_1$ , wherein M\* has the same meaning as M and  $X'_1$  has the same meaning as  $X_1$  where such dimeric compounds which are precursors  
20 to the cationic portion of the catalyst are represented by the formula:



w is an integer from 0 to 3;

30 B is a chemically stable, non-nucleophilic anionic complex having a molecular diameter about or greater than 4 angstroms or an anionic Lewis-acid activator resulting from the reaction of a Lewis-acid activator with the precursor to the cationic portion of the catalyst system described in formulae 1-4. When B' is 35 a Lewis-acid activator,  $X_1$  can also be an alkyl group donated by the Lewis-acid activator; and

d is an integer representing the charge of B.

The improved catalysts are preferably prepared by combining at least two components. In one preferred method, the first component is a cyclopentadienyl derivative of a Group 4 metal compound containing at 5 least one ligand which will combine with the second component or at least a portion thereof such as a cation portion thereof. The second component is an ion-exchange compound comprising a cation which will irreversibly react with at least one ligand contained. 10 in said Group 4 metal compound (first component) and a non-coordinating anion which is either a single coordination complex comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central formally charge-bearing metal or 15 metalloid atom or an anion comprising a plurality of boron atoms such as polyhedral boranes, carboranes and metallacarboranes.

In general, suitable anions for the second component may be any stable and bulky anionic complex 20 having the following molecular attributes: 1) the anion should have a molecular diameter greater than 4 Å; 2) the anion should form stable ammonium salts; 3) the negative charge on the anion should be delocalized over the framework of the anion or be localized within 25 the core of the anion; 4) the anion should be a relatively poor nucleophile; and 5) the anion should not be a powerful reducing to oxidizing agent. Anions meeting these criteria - such as polynuclear boranes, 30 carboranes, metallacarboranes, polyoxoanions and anionic coordination complexes are well described in the chemical literature.

The cation portion of the second component may comprise Bronsted acids such as protons or protonated Lewis bases or may comprise reducible Lewis acids such 35 as ferricinium, tropylium, triphenylcarbenium or silver cations.

In another preferred method, the second component is a Lewis-acid complex which will react with at least one ligand of the first component, thereby forming an ionic species described in formulae 1-4 with the ligand abstracted from the first component now bound to the second component. Alumoxanes and especially methylalumoxane, the product formed from the reaction of trimethylaluminum in an aliphatic or aromatic hydrocarbon with stoichiometric quantities of water, are particularly preferred Lewis-acid second components.

Upon combination of the first and second components, the second component reacts with one of the ligands of the first component, thereby generating an ion pair consisting of a Group 4 metal cation and the aforementioned anion, which anion is compatible with and "non-coordinating" toward the Group 4 metal cation formed from the first component. The anion of the second compound must be capable of stabilizing the Group 4 metal cation's ability to function as a catalyst and must be sufficiently labile to permit displacement by an olefin, diolefin or an acetylenically unsaturated monomer during polymerization. The catalysts of this invention may be supported. U.S. Patents 4,808,561, issued 2-28-89; 4,897,455 issued 1-3-90; 5,057,475 issued 10-15-91; and U.S. Patent Application 459,921 (published as PCT International publication WO 91/09882) disclose such supported catalysts and the methods to produce such and are herein incorporated by reference.

#### A. The Metallocene Component

The Group 4 metal compounds; i.e., titanium, zirconium, and hafnium metallocene compounds, useful as first compounds in the preparation of the improved catalyst of this invention are cyclopentadienyl derivatives of titanium, zirconium and hafnium. In

general, useful titanocenes, zirconocenes, and hafnocenes may be represented by the following general formulae:

5.  $(A-Cp)MX_1X_2$   
 6.  $(A-Cp)ML$   
 7.  $(Cp^*)(CpR)MX_1$   
 8.  $(C_5H_{5-y-x}S_x)$

10  $(A')_y$   $M$   $X_1$   $(L')_v$   
 $(JS'_{z-1-y})$   $X_2$

wherein:

15  $(A-Cp)$  is either  $(Cp)(Cp^*)$  or  $Cp-A'-Cp^*$ ; Cp and  $Cp^*$  are the same or different cyclopentadienyl rings substituted with from zero to five substituent groups S, each substituent group S being, independently, a radical group which is a hydrocarbyl, substituted-  
 20 hydrocarbyl, halocarbyl, substituted-halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 elements, substituted Group 16 elements or halogen radicals, or Cp and  $Cp^*$  are  
 25 cyclopentadienyl rings in which any two adjacent S groups are joined forming a  $C_4$  to  $C_{20}$  ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

30 R is a substituent on one of the cyclopentadienyl radicals which is also bonded to the metal atom;

35  $A'$  is a bridging group, which group may serve to restrict rotation of the Cp and  $Cp^*$  rings or  $(C_5H_{5-y-x}S_x)$  and  $JS'_{(z-1-y)}$  groups;

$y$  is 0 or 1;

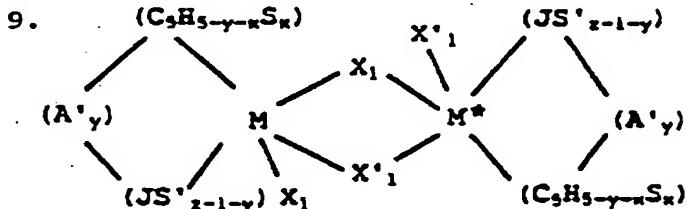
35  $(C_5H_{5-y-x}S_x)$  is a cyclopentadienyl ring substituted with from zero to five S radicals;

$x$  is from 1 to 5 denoting the degree of substitution;

$(JS_{z-1-y})$  is a heteroatom ligand in which  $J$  is an element from Group 15 of the Periodic Table of Elements 5 with a coordination number of 3 or an element from Group 16 with a coordination number of 2,  $S$  is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, or halocarbyl-10 substituted organometalloid; and  $z$  is the coordination number of the element  $J$ ;

$L$  is an olefin, diolefin or aryne ligand, or a neutral Lewis base;  $L'$  can also be a second transition metal compound of the same type such that the two metal centers  $M$  and  $M^*$  are bridged by  $X_1$  and  $X'^1$ , wherein  $M^*$  has the same meaning as  $M$  and  $X'^1$  has the same meaning as  $X_1$  where such dimeric compounds which are precursors 15 to the cationic portion of the catalyst are represented by formula 4;

20



25

wherein:

$w$  is an integer from 0 to 3; and  
 $X_1$  and  $X_2$  are, independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, 30 halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, disubstituted Group 15 element radicals, or substituted Group 16 element radicals; or  $X_1$  and  $X_2$  are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or  $X_1$  and  $X_2$  together 35 can be an olefin, diolefin or aryne ligand; or when

Lewis-acid activators are used,  $X_1$  and  $X_2$  can also be joined to form a anionic chelating ligand or can independently be any mono-valent anionic ligand including halides.

5 Table 1 depicts representative constituent moieties for the metallocene components of formulae 6-9. The list is for illustrative purposes only and should not be construed to be limiting in any way. A number of final components may be formed by permuting  
10 all possible combinations of the constituent moieties with each other. Illustrative compounds of the formula 6 type are: bis(cyclopentadienyl)hafnium dimethyl, ethylenebis(tetrahydroindenyl)zirconium dihydride, bis(pentamethyl)zirconium ethylidene, dimethylsilyl(1-fluorenyl)(cyclopentadienyl)titanium dichloride and the like. Illustrative compounds of the formula 7 type  
15 are: bis(cyclopentadienyl) (1,3-butadiene(zirconium), bis(cyclopentadienyl) (2,3-dimethyl-1,3-butadiene) zirconium, bis(pentamethylcyclopentadienyl) (benzene) zirconium, bis(pentamethylcyclopentadienyl) titanium ethylene and the like. Illustrative compounds of the formula 8 type are: (pentamethylcyclopentadienyl) (tetramethylcyclopentadienylmethylenes) zirconium hydride, (pentamethylcyclopentadienyl)  
20 (tetramethylcyclopentadienyl)- (tetramethylcyclopentadienylmethylenes) zirconium phenyl and the like. Illustrative compounds of the formula 9 type are: dimethylsilyl(tetramethylcyclopentadienyl) (t-butylamido)zirconium dichloride,  
25 ethylene(methylcyclopentadienyl) (phenylamido)titanium dimethyl,  
30 methylphenylsilyl(indenyl) (phenyphosphido)hafnium dihydride and (pentamethylcyclopentadienyl) (di-t-butylamido)hafnium dimethoxide.

For illustrative purposes, the above compounds and those permuted from Table 1 include the neutral Lewis base ligand (L'). The conditions under which complexes containing neutral Lewis base ligands such as ether or 5 those which form dimeric compounds is determined by the steric bulk of the ligands about the metal center. For example, the t-butyl group in  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$  has greater steric requirements than the phenyl group 10 in  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{NPh})\text{ZrCl}_2\text{Et}_2\text{O}$  thereby not permitting ether coordination in the former compound in its solid state. Similarly, due to the decreased steric bulk of the trimethylsilylcyclopentadienyl group in 15  $[\text{Me}_2\text{Si}(\text{Me}_3\text{SiC}_5\text{H}_3)(\text{N-t-Bu})\text{ZrCl}_2]_2$  versus that of the tetramethylcyclopentadienyl group in  $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-t-Bu})\text{ZrCl}_2$ , the former compound is dimeric and the latter is not.

TABLE I

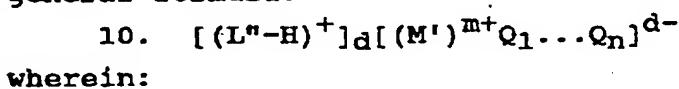
$\text{[C}_5\text{H}_5\text{-y-x]_5\text{x}_1}$	$\text{[C}_5\text{H}_5\text{-y-x]_5\text{x}_1}$	$\text{[3S'-z-y]}$	$\text{[B - Lewis Acid)}$	$\text{x}_1 \text{ or } \text{x}_2 \text{ Acid)$	$\text{H}$
dimethylsilyl	cyclopentadienyl	t-butylamido	hydride		zirconium
diethylsilyl	1,4-dimethylcyclopentadienyl	phenylamido	methyl		hafnium
di-n-propylsilyl	2,5-dimethylcyclopentadienyl	p-n-butyphenylamido	ethyl		titanium
di-isopropylsilyl	2-indenyl	cyclohexylamido	phenyl		
di-n-butylsilyl	3,4-diethylcyclopentadienyl	perfluorophenylamido			
di-t-butylsilyl	2,5-diethylcyclopentadienyl	n-butylamido			
di-n-hexylsilyl	tetramethylcyclopentadienyl	methylamido			
methyldiphenylsilyl	tetraethylcyclopentadienyl	ethylamido			
ethylmethyldiphenylsilyl	tetraphenylcyclopentadienyl	n-propylamido			
diphenylsilyl	tetra-n-propylcyclopentadienyl	isopropylamido			
di-(p-t-butylphenylsilyl)	3,4-di-n-butylcyclopentadienyl	benzylamido	hexyl		
n-hexylmethylsilyl	3,4-dicyclohexylcyclopentadienyl	cyclododecylamido	isobutyl		
cyclopentanthylenesilyl	2,5-di-n-butylcyclopentadienyl	s-butylamido	heptyl		
cycloketotetraethylenesilyl	2,5-dicyclohexylcyclopentadienyl	t-butylphosphido	octyl		
cyclotrimethylenelesilyl	3-n-octyl-4-n-hexylcyclopentadienyl	ethylphosphido	nonyl		
cyclohexylmethylenesilyl	2-tetrahydroindenyl	phenylphosphido	decyl		
dimethylgeranyl	3-isopropyl-4-t-butylcyclopentadienyl	cyclohexylphosphido	etyl		
diethylgeranyl	3-phenyl-4-benzylcyclopentadienyl	oxo	chloro		
phenylamido	3,4-diphenylcyclopentadienyl	aurido	fluoro		
t-butylamido	2,5-diphenylcyclopentadienyl	methoxide	bromo		
methyldiphenylsilyl	2,5-diphenylcyclopentadienyl	ethoxide	iodo		
t-butyldiphenylsilyl	3,4-bis(trimethylsilyl)cyclopentadienyl	methyldithio	methoxy		
ethyldiphenylsilyl	3,4-bis(trimethylsilyl)cyclopentadienyl	ethylthio	ethoxy		
phenyldiphenylsilyl	3,4-bis(trimethylsilyl)cyclopentadienyl	dimethylamide	propoxy		
dimethylmethylenesilyl	3,4-bis(trimethylsilyl)cyclopentadienyl	phenylamide	butoxy		
diethylmethylenesilyl	2,5-bis(triethylplumbyl)cyclopentadienyl	methylphenylamide	phenoxy		
ethylene	2-ethyl-5-n-propylcyclopentadienyl	dimethylamido	dimethylamido		
dimethylmethylenesilyl	2-methyl-5-t-butylcyclopentadienyl	diethylamido	diethylamido		
diisopropylmethylenesilyl	2,5-bis(trimethylsilyl)cyclopentadienyl	methylethylamido	methylethylamido		
propylene	3,4-bis(trimethylsilyl)cyclopentadienyl	diphenylamido	diphenylamido		
dimethylpropylene	3,4-bis(N,N-dimethylamido)-cyclopentadienyl	dicyclohexylphosphido	dicyclohexylphosphido		
diethylpropylene	3,4-bis(trimethylsilyl)cyclopentadienyl	dimethyloxy	dimethyloxy		
1,1-dimethyl-3,3-dimethyl	3,4-bis(trimethylsilyl)cyclopentadienyl	dimethyloxy	dimethyloxy		
propylene	3,4-bis(trimethylsilyl)cyclopentadienyl	dimethyloxy	dimethyloxy		
tetramethylidisiloxane	3,4-dimethylcyclopentadienyl	dimethyloxy	dimethyloxy		
1,1,4,4-tetramethylsilyl	2,5-dimethoxycyclopentadienyl	dimethyloxy	dimethyloxy		
ethylene	2,5-dimethyl-3,4-diethylcyclopentadienyl	dimethyloxy	dimethyloxy		
	2,5-dimethyl-3,4-dimethylcyclopentadienyl	dimethyloxy	dimethyloxy		
	2,5-dimethyl-3,4-dimethylcyclopentadienyl	dimethyloxy	dimethyloxy		

**B. The Activator Component**

Ionic catalysts can be prepared by reacting a transition metal compound with some neutral Lewis acids, such as  $B(C_6F_6)_3$  or an alumoxane, which upon 5 reaction with the hydrolyzable ligand (X) of the transition metal compound forms an anion, such as  $([B(C_6F_5)_3(X)]^-)$ , which stabilizes the cationic transition metal species generated by the reaction. Ionic catalysts can be, and preferably are, 10 prepared with activator components which are ionic compounds or compositions.

Compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process of this invention comprise a cation, which is 15 preferably a Bronsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species (the Group 4 cation), which is formed when the two compounds are 20 combined and said anion will be sufficiently labile to be displaced by olefinic diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Two classes of compatible non-coordinating anions have been disclosed 25 in copending U.S. Patent Application Nos. 133,052 and 133,480: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a plurality of boron atoms such as carboranes, 30 metallacarboranes and boranes.

In general, the activator compounds containing single anionic coordination complexes which are useful in this invention may be represented by the following 35 general formula:



H is a hydrogen atom;

[L"-H] is a Bronsted acid;

M' is a metal or metalloid;

Q<sub>1</sub> to Q<sub>n</sub> are, independently, bridged or unbridged  
5 hydride radicals, dialkylamido radicals, alkoxide and  
aryloxide radicals, hydrocarbyl and substituted-  
hydrocarbyl radicals, halocarbyl and substituted-  
halocarbyl radicals and hydrocarbyl and halocarbyl-  
substituted organometalloid radicals and any one, but  
10 not more than one, of Q<sub>1</sub> to Q<sub>n</sub> may be a halide radical;

10 m is an integer representing the formal valence  
charge of M; and

n is the total number of ligands q.

As indicated above, any metal or metalloid capable of  
15 forming an anionic complex which is stable in water may  
be used or contained in the anion of the second  
compound. Suitable metals, then, include, but are not  
limited to, aluminum, gold, platinum and the like.  
Suitable metalloids include, but are not limited to,  
20 boron, phosphorus, silicon and the like. Compounds  
containing anions which comprise coordination complexes  
containing a single metal or metalloid atom are, of  
course, well known and many, particularly such  
compounds containing a single boron atom in the anion  
25 portion, are available commercially. In light of this,  
salts containing anions comprising a coordination  
complex containing a single boron atom are preferred.

The preferred activator compounds comprising boron  
may be represented by the following general formula:

30 11. [L"-H]<sup>+</sup>[BAr<sub>1</sub>Ar<sub>2</sub>X<sub>3</sub>X<sub>4</sub>]<sup>-</sup>

wherein:

B is a boron in a valence state of 3;

Ar<sub>1</sub> and Ar<sub>2</sub> are the same or different aromatic or  
substituted-aromatic hydrocarbon radicals containing  
35 from about 6 to about 20 carbon atoms and may be linked  
to each other through a stable bridging group; and

$X_3$  and  $X_4$  are, independently, hydride radicals, hydrocarbyl and substituted-hydrocarbyl radicals, halocarbyl and substituted-halocarbyl radicals, hydrocarbyl- and halocarbyl-substituted organometalloid 5 radicals, disubstituted Group 15 element radicals, substituted Group 16 element radicals and halide radicals, with the proviso that  $X_3$  and  $X_4$  will not be halide at the same time.

In general,  $Ar_1$  and  $Ar_2$  may, independently, be any 10 aromatic or substituted-aromatic hydrocarbon radical. Suitable aromatic radicals include, but are not limited to, phenyl, naphthyl and anthracenyl radicals. Suitable substituents on the substituted-aromatic hydrocarbon radicals, include, but are not necessarily 15 limited to, hydrocarbyl radicals, organometalloid radicals, alkoxy and aryloxy radicals, alkylamido radicals, fluorocarbyl and fluorohydrocarbyl radicals and the like such as those useful as  $X_3$  and  $X_4$ . The substituent may be ortho, meta or para, relative to the 20 carbon atoms bonded to the boron atom. When either or both  $X_3$  and  $X_4$  are a hydrocarbyl radical, each may be the same or a different aromatic or substituted-aromatic radical as are  $Ar_1$  and  $Ar_2$ , or the same may be a straight or branched alkyl, alkenyl or alkynyl 25 radical, a cyclic hydrocarbon radical or an alkyl-substituted cyclic hydrocarbon radical.  $X_3$  and  $X_4$  may also, independently be alkoxy or dialkylamido radicals wherein the alkyl portion of said alkoxy and dialkylamido radicals, hydrocarbyl radicals and 30 organometalloid radicals and the like. As indicated above,  $Ar_1$  and  $Ar_2$  could be linked to either  $X_3$  or  $X_4$ . Finally,  $X_3$  and  $X_4$  may also be linked to each other through a suitable bridging group.

Illustrative, but non-limiting, examples of boron 35 compounds which may be used as an activator component in the preparation of the improved catalysts of this invention are trialkyl-substituted ammonium salts such

as triethylammonium tetra(phenyl)boron,  
tripropylammonium tetra(phenyl)boron, tri(n-  
butyl)ammonium tetra(phenyl)boron, trimethylammonium  
tetra(p-tolyl)boron, trimethylammonium tetra(o-  
5 tolyl)boron, tributylammonium  
tetra(pentafluorophenyl)boron, tripropylammonium  
tetra(o,p-dimethylphenyl)boron, tributylammonium te-  
tra(m,m-dimethylphenyl)boron, tributylammoniumtetra(p-  
tri-fluoromethylphenyl)boron, tri(n-butyl)ammonium  
10 tetra(o-tolyl)boron and the like; N,N-dialkyl anilinium  
salts such as N,N-dimethylanilinium  
tetra(pentafluorophenyl)boron, N,N-diethylanilinium  
tetra(phenyl)boron, N,N-2,4,5-pentamethylanilinium  
tetra(phenyl)boron and the like; dialkyl ammonium salts  
15 such as di(i-propyl)ammonium  
tetra(pentafluorophenyl)boron, dicyclohexylammonium  
tetra(phenyl)boron and the like; and triaryl  
phosphonium salts such as triphenylphosphonium  
tetra(phenyl)boron, tri(methylphenyl)phosphonium  
20 tetra(phenyl)boron, tri(dimethylphenyl)phosphonium  
tetra(phenyl)boron and the like.

Similar lists of suitable compounds containing  
other metals and metalloids which are useful as  
activator components may be made, but such lists are  
25 not deemed necessary to a complete disclosure. In this  
regard, it should be noted that the foregoing list is  
not intended to be exhaustive and that other useful  
boron compounds as well as useful compounds containing  
other metals or metalloids would be readily apparent to  
30 those skilled in the art from the foregoing general  
equations.

The most preferred activator compounds comprising  
boron may be represented by the following general  
formula:



wherein:

F is fluorine, C is carbon and B, L', and Q are defined hereinabove. Illustrative but not limiting, examples of most preferred activator compounds

5 comprising boron which may be used in the preparation of the improved catalysts of this invention include N,N-dialkylanilinium salts (L' = N,N-dialkylaniline) where Q is a simple hydrocarbyl such as methyl, butyl, cyclohexyl, or phenyl or where Q is a polymeric 10 hydrocarbyl of indefinite chain length such as polystyrene, polyisoprene, or poly-paramethylstyrene. Polymeric Q substituents on the most preferred anion offer the advantage of providing a highly soluble ion-exchange activator component and final ionic catalyst.

15 Soluble catalysts and/or precursors are often preferred over insoluble waxes, oils, phases, or solids because they can be diluted to a desired concentration and can be transferred easily using simple equipment in commercial processes.

20 Activator components based on anions which contain a plurality of boron atoms may be represented by the following general formulae:

13.  $[L''-H]c[(CX)a(BX)mX_b]^{c-}$  or

14.  $[L''-H]d'[[[(CX_6)_a'(BX_7)_m'(X_8)_b']]^{c'-}]_2M^{n'+}d'^-$

25 wherein

$[L''-H]$  is either  $H^+$  or a Bronsted acid derived from the protonation of a neutral Lewis base;

30 X, X', X'', X<sub>6</sub>, X<sub>7</sub> and X<sub>8</sub> are, independently, hydride radicals, halide radicals, hydrocarbyl radicals, substituted-hydrocarbyl radicals, halocarbyl radicals, substituted-halocarbyl radicals, or hydrocarbyl- or halocarbyl-substituted organometalloid radicals;

M is a transition metal;

35 a and b are integers  $\geq 0$ ; c is an integer  $\geq 1$ ; a<sub>a</sub>+b<sub>a</sub>+ c<sub>a</sub>= an even-numbered integer from 2 to about 8; and m is an integer ranging from 5 to about 22;

a and b are the same or a different integer 0; c is an integer  $\geq 2$ ; a + b + c = an even-numbered integer from 4 to about 8; m is an integer from 6 to about 12; n is an integer such that  $2c - n = d$ ; and d is an 5 integer  $\geq 1$ .

Preferred anions of this invention comprising a plurality of boron atoms comprise:

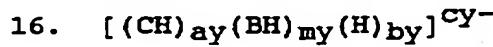
(1) A trisubstituted ammonium salt of a borane or carborane anion satisfying the general formula:



wherein:

$ax$  is either 0 or 1;  $cx$  is either 1 or 2;  $ax + cx = 2$ ; and  $bx$  is an integer ranging from about 10 to 12;

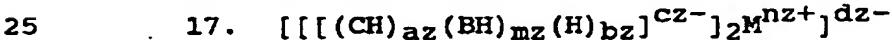
15 (2) A trisubstituted ammonium salt of a borane or carborane or a neutral borane or carborane compound satisfying the general formula:



wherein:

20  $ay$  is an integer from 0 to 2;  $by$  is an integer from 0 to 3;  $cy$  is an integer from 0 to 3;  $ay + by + cy = 4$ ; and  $my$  is an integer from about 9 to about 18; or

(3) A trisubstituted ammonium salt of a metallaborane or metallacarborane anion satisfying the following general formula:



wherein:

30  $az$  is an integer from 0 to 2;  $bz$  is an integer from 0 to 2;  $cz$  is either 2 or 3;  $mz$  is an integer from about 9 to 11;  $az + bz + cz = 4$ ; and  $nz$  and  $dz$  are, respectively, 2 and 2 or 3 and 1.

Illustrative, but not limiting, examples of second components which can be used in preparing catalyst systems utilized in the process of this invention wherein the anion of the second component contains a plurality of boron atoms (as in formulae 10-17) are mono-, di-, trialkylammonium and phosphonium and dialkylarylammonium and -phosphonium salts such as

5       bis[tri(n-butyl)ammonium] dodecaborate, bis[tri(n-butyl)ammonium]decachlorodecaborate, tri(n-butyl)ammonium dodecachlorododecaborate, tri(n-butyl)ammonium 1-carbadecaborate, tri(n-butyl)ammonium 10 1-carbaundecaborate, tri(n-butyl)ammonium 1-carbadodecaborate, tri(n-butyl)ammonium 1-trimethylsilyl-1-carbadecaborate, tri(n-butyl)ammonium dibromo-1-carbadodecaborate; borane and carborane complexes and salts of borane and carborane anions such 15 as decaborane(14), 7,8-dicarbaundecaborane(13), 2,7-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane, tri(n-butyl)ammonium 6-carbadecaborate(12), tri(n-butyl)ammonium 7-carbaundecaborate, tri(n-butyl)ammonium 7,8-20 dicarbaundecaborate and metallaborane anions such as tri(n-butyl)ammonium bis(nonahydrido-1,3-dicarbanaborate)cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)nikelate(III), tri(n-butyl)ammonium bis(nonahydrido-25 7,8-dimethyl-7,8-dicarbaundecaborato)ferrate(III), tri(n-butyl)ammonium bis(tribromo-octahydrido-7,8-dicarbaundecaborato)cobaltate(III), tri(n-butyl)ammonium bis(undecahydrido-7-carbaundecaborato)cobaltate(III). A similar list of representative phosphonium compounds 30 can be recited as illustrative second compounds, but for the sake of brevity, it is simply noted that the phosphonium and substituted-phosphonium salts corresponding to the listed ammonium and substituted-ammonium salts could be used as second compounds in the 35 present invention.

The preferred activator compounds comprising Lewis-acid activators and in particular alumoxanes are represented by the following general formulae:

5            18.  $(R^3-Al-O)_p$   
          19.  $R^4(R^5-Al-O)_p-AlR^6_2$   
          20.  $(M')^{m+}Q'^m$

An alumoxane is generally a mixture of both the linear and cyclic compounds. In the general alumoxane formula,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are, independently a  $C_1-C_6$  10 alkyl radical, for example, methyl, ethyl, propyl, butyl or pentyl and "p" is an integer from 1 to about 50. Most preferably,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  are, each 15 methyl and "p" is at least 4. When an alkyl aluminum halide is employed in the preparation of the alumoxane, one or more  $R^{3-6}$  groups may be halide.  $M'$  and  $M$  are as 20 described previously and  $Q'$  is a partially or fully fluorinated hydrocarbyl.

As is now well known, alumoxanes can be prepared by various procedures. For example, a trialkyl 25 aluminum may be reacted with water, in the form of a moist inert organic solvent; or the trialkyl aluminum may be contacted with a hydrated salt, such as hydrated copper sulfate suspended in an inert organic solvent, to yield an alumoxane. Generally, however prepared, the reaction of a trialkyl aluminum with a limited 30 amount of water yields a mixture of both linear and cyclic species of alumoxane.

Suitable alumoxanes which may be utilized in the catalyst systems of this invention are those prepared 35 by the hydrolysis of a trialkylaluminum, such as trimethylaluminum, triethylaluminum, tripropylaluminum, triisobutylaluminum, dimethylaluminum chloride, diisobutylaluminum chloride, diethylaluminum chloride and the like. The most preferred alumoxane for use is methylalumoxane (MAO). Methylalumoxanes having an average degree of oligomerization of from 4 to 25 ("p")

= 4 to 25), with a range of 13 to 25 are the most preferred.

It is recognized that an alumoxane is not a discrete material. A typical alumoxane will contain 5 free trisubstituted or trialkyl aluminum, bound trisubstituted or trialkyl aluminum, and alumoxane molecules of varying degree of oligomerization. Those methylalumoxanes most preferred contain lower levels of trimethylaluminum. Lower levels of trimethylaluminum 10 can be achieved by reaction of the trimethylaluminum with a Lewis base or by vacuum distillation of the trimethyl aluminum or any other means known in the art.

It is also recognized that after reaction with the transition metal compound, some alumoxane molecules 15 are in the anionic form as represented by equations 1-3, and thus for our purposes, are considered "non-coordinating" anions.

The activator compositions most preferred for forming the ionic catalyst used in this process are 20 those containing a tetrapentafluorophenyl boron anion; two or more tripentafluorophenyl boron anion groups covalently bond to a central atomic molecular or polymeric complex or particle; tripentafluorophenyl boron; or methylalumoxane.

25 Other examples of activator specific compositions which may be used to form an anionic catalyst useful in this invention are identified and more fully described in European Patent Application Nos. 0 277 003 and 0 277 004 and WO 92/00333 which are hereby incorporated by 30 reference.

#### CHOICE OF CATALYST

This invention relates to a process to produce 35 long chain branched polymers, to catalysts used to produce long chain branched polymers and to the polymers themselves. This invention relates to a method for producing polymers with substantially linear

long chain branching comprising contacting, under polymerization conditions, a vinyl terminated polymer (macromonomer) with a chain length of 250 or more carbons, with one or more olefin monomers and a 5 metallocene catalyst system comprising a mono, di, or tri cyclopentadienyl transition metal catalyst cocatalyzed with a non-coordinating anion or an alumoxane or a Lewis acid activator. This invention also contemplates a process for producing a branched 10 polymer comprising:

contacting in the presence of a polymerization catalyst system,

(i) a macromonomer at least 250 carbons long comprising one or more C<sub>2</sub>-C<sub>30</sub> olefinic monomer units 15 said macromonomer having chain end vinyl unsaturation, and

(ii) a polymerizable olefinic monomer or monomer mixture

under conditions to (co)polymerize the monomers 20 and incorporate the macromonomer into the growing (co)polymer chain via the chain end unsaturation, said catalyst system comprising mono-, di-, or tri- cyclopentadienyl transition metal catalyst cocatalyzed with a non-coordinating anion, an aluminium 25 alkyl, or an alumoxane.

The reaction is maintained at 70°C, more preferably 70 to 100°C, even more preferably at 90°C. The weight ratio of macromonomer to olefin monomer present is between about 1:1 to about 1:5, preferably about 1:1.5 to about 1:3, more preferably about 1:2. 30

The branched polymers of this invention are comprised of a family of polyolefins and olefin copolymers which are copolymerizable by metallocene polymerization. Long chain branched polymers of this 35 type are made by copolymerization of vinyl terminated polymers with the desired ethylenically unsaturated monomer or monomers. The family of polyolefins

includes low to high density polyethylene or ethylene-alpha-olefin copolymers as well as polypropylene and polypropylene copolymers. The vinyl terminated polymers useful in this invention include high density 5 polyethylene and polyethylene copolymers. Production of these polymers gives control over the side-chain molecular weight and composition. The branched polymers of this invention can be a low-density polyethylene with a high-density polyethylene branch. 10 They are also not limited to side-chains consisting of the same polymer composition as the backbone. Likewise it is contemplated that the macromonomers can comprise homopolymers or copolymers of olefins, particularly of C<sub>2</sub> to C<sub>30</sub> alpha olefins. Specifically a copolymer or 15 polymer with more than 250 carbons that has vinyl termination can be used. The metallocene catalysts disclosed in this invention can produce vinyl-terminated homopolymers and copolymers. However, another method to produce vinyl termination is to 20 produce a polymer with an ethylene "cap" or end with the needed vinyl group. This could be accomplished by raising the reaction temperature at the "end" of the reaction and simultaneously adding ethylene so that the ethylene preferentially polymerizes to form an end 25 "cap" or block. A block copolymer of ethylene and a C<sub>3</sub> to C<sub>30</sub> alpha olefin would also present the necessary vinyl termination.

The main chain and the sidechains may be the same of different olefin homo or copolymers. In particular 30 main and side chains of ethylene are preferred. However main and side chains of ethylene copolymerized with propylene, 1-butene, 1-pentene, 4-methylpentene-1, 1-hexene or 1-octene are also preferred.

The ability to prepare long-chain branched olefins 35 in which the side-chain compositions are significantly different from the backbone adds a unique dimension to the polymers of this invention

The branched polymers of this invention typically have a weight average molecular weight at or above 50,000, preferably 50,000 to 1,000,000 and a Mw/Mn of 6 or less. The vinyl terminated polymers (macromers) 5 that become the side chains in the branched polymers of this invention are typically more than 200 carbons long, preferably 250 to 3500, even more preferably 300 to 3000 carbons long. Further these side chains insert into the main chain at an average of up to 5 side 10 chains per 1000 main chain carbons, although it is statistically possible for a particular main chain to have no side chains. Also, as a benefit of utilizing titanium-containing monocyclopentadienyl transition metal catalysts in the catalyst system, a narrow 15 composition distribution of the side chains may be obtained. A narrow composition distribution means that among the individual polymer main chains the number of side chains are roughly similar. For example, three main chains with 2, 3, and 2 side chains respectively 20 have a very narrow composition distribution, while three main chains with 3, 9, and 20 sides chains, respectively, have a broad composition distribution. As an added benefit, if the main chain is a copolymer made 25 using a titanium containing monocyclopentadienyl metallocene catalyst, it will have a narrow composition distribution and higher comonomer incorporation than traditional coordination catalysts.

It is also contemplated by this invention that the vinyl terminated macromonomer can be produced in one 30 step of a continuous or series process which then proceeds to copolymerize the macromonomer with one or more alpha olefins. It is also contemplated that the macromonomer can be produced separately by one process and then polymerized later in a separate similar or 35 different process.

CATALYSTS TO PRODUCE POLYMERS OF THE MACROMONOMER AND  
AN OLEFIN

A large group of metallocene catalysts may be selected from to produce both the vinyl terminated polymers (macromers) and the branched polymers of this invention. The choice of catalyst system is influenced by the characteristics desired in the final product.

5 For example, a noncoordinating anion activation system rather than MAO could be found to be preferable to

10 avoid isomerization problems, or the metallocene catalyst  $Cp_2ZrMe_2$  (bis cyclopentadienyl zirconium dimethyl) with  $(pfp)_3B$  (perfluorotriphenyl boron) as the cocatalyst activator could be chosen because of this system's high activity at higher temperatures such

15 as 90°C and above. Further this catalyst system gives high levels of vinyl ends during polymerization in hexane and few or no vinyl ends when polymerized in toluene. The resulting vinyl terminated polymers are branched. This branching can be eliminated if a

20 sterically hindered catalyst like  $(Me_5Cp)_2ZrMe_2$  (bis pentamethylcyclopentadienyl zirconium dimethyl) is used. This catalyst system sterically inhibits the copolymerization of vinyl terminated polymers. It should be noted that the vinyl terminated macromonomers.

25 of this invention can be branched. However the level of this branching does not approach a dendritic structure. These macromers and those that have little or no side chain branching or are substantially linear will be referred to as linear.

30 The catalyst choices for copolymerization of vinyl terminated polymers with other monomers are also large and include catalyst systems containing bridged and unbridged bis cyclopentadienyl transition metal compounds as well as monocyclopentadienyl transition

35 metal compounds. Monocyclopentadienyl transition metal catalysts are preferred as they polymerize large "monomers" well. For example, monocyclopentadienyl

(Mono Cp) transition metal catalysts, particularly titanium, incorporate more monomer than coordination catalysts. Thus one would choose a Mono Cp Ti catalyst to make lower density products over the

5 Tris(perfluorophenyl)Boron activated systems utilized in example 1 and 2 to make high density material.

To understand the advantages of polymers produced in accordance with the present invention, some general discussions of the properties of polymer solids and

10 melts is helpful. Molten polyethylene is highly viscous. The viscosity is a function of weight-average molecular weight ( $M_w$ ); molecular weight distribution ( $M_w/M_n$ ), also called the index of polydispersity; and the shear rate exerted on the polymer. The molecular

15 weight values are in part related to branching of the polymer. Molten polyethylene is classified as a pseudoplastic fluid, which means that its viscosity decreases with increasing shear rate. The relationship between viscosity and shear rate depends upon the

20 molecular weight distribution and degree of long chain branching of the polymer. Polymers having a broad molecular weight distribution tend to have lower viscosity values at conditions of high shear rates than polymers having a narrow molecular weight distribution

25 while having equivalent viscosities at conditions of low shear rates.

As noted, viscosity as a function of shear rate is also dependent upon the degree of long chain branching of a polymer which affects molecular weight

30 distribution. In general, a polymer with long chain branching will have higher viscosity values at low shear rates and lower viscosity values at high shear rates compared to an unbranched polymer with equivalent molecular weight. Lower viscosity at high shear rates means the long chain branched polymer can be extruded at lower temperatures and at a higher rate which

35 results in less energy consumption.

From a processability viewpoint, it is usually desirable to have a polymer which displays high viscosity at low shear rates and low viscosity at high shear rates, in other words, it is desirable to have a 5 polymer that processes with the characteristics of a branched polymer at conditions of low shear while having the processing characteristics of a broad molecular weight distribution branched polymer at conditions of high shear. This combination of 10 properties is often sought by broadening the molecular weight distribution of a polymer by introducing long chain branching.

The inventors have found that the positive viscosity processing characteristics of a polymer at 15 both ends of the shear rate range may be achieved by polymers in accordance with the present invention. The predictable solid polymer mechanical properties achievable by polymers in accordance with the present invention are good impact and tear resistance, good 20 environmental stress crack resistance (ESCR) values, good tensile properties, good modulus/density balance, good reblock/density balance, and good clarity, relative to linear polyethylenes without long chain branching.

25 This unique balance of favorable polymer melt processability and solid polymer mechanical characteristics is achieved through the creation of remote long chain branching at a frequency and length great enough to impart processability characteristics 30 of LDPEs but at a low enough frequency so as not to destroy the superior solid polymer physical characteristics of LPEs. In particular, this balance is achieved by the introduction of some linear long chain branches having a average molecular weight 35 greater than the critical molecular weight for entanglement ( $M_c$ ) of the polymer with a linear long chain branching frequency less than 5.0 branches per

1,000 carbon atoms of the main polymer chains. These polymers may be produced over a wide range of molecular weight distributions ( $M_w/M_n$ ) (index of polydispersity) of 2.0 to 10. Preferably, the frequency of long chain branching is less than 5 branches per 1,000 carbon atoms of the main polymer chains (preferably an average frequency of 0.2 to 3 chains per 1000 C, atom, even more preferably an average frequency of 0.9 to 2 chains per 1000 C, even more preferably an average frequency of 1 to 2 chains per 1000 C) with a preferred molecular weight distribution range of about 2 to about 6, more preferably 2 to 4.

These advantageous properties can be achieved when even 5 or more weight percent of the composition is "branched." This may occur when a branched polymer is blended with another polymer or when the branched polymer is part of a reactor blend. Preferably the branched polymer is present at least 5 weight percent, even more preferably at least 10 weight percent, even more preferably at least 40 to 70 weight percent.

The viscosity characteristics of polymers of the present invention are not the only processing advantages. Another advantage of polymers having linear long chain branching in accordance with the present invention are the superior elastic characteristics of the polymer melt. Molten polyethylene exhibits elastic properties over a wide temperature range. After molten polyethylene passes through the die of an extruder under pressure, the strand of polyethylene increases in diameter or thickness. This is known as extrudate swell. At low shear rates, extrudate swell increases as molecular weight and long chain branching increase. In other words, extrudates typically swell as molecular weight distribution broadens.

Polymers produced in accordance with the present invention exhibit increased extrudate swell. The

significance of this increased extrudate swell is that is a reflection of what is known as the elastic nature of the polymer. The elastic nature of the polymer is very important in certain polymer melt extrusion processes such as the manufacture of tubular film, chill roll casting and extrusion coating in which an extruded web of film is produced which is stretched in the direction of flow. Such extrusion processes can only be carried out with materials that are able to sustain a tensile stress on the melt. In other words, it is important that the polymer melt be somewhat elastic. There should be a balance between the elasticity of the polymer melt and the viscosity in blow molding operation. The balance between elasticity and viscosity of the polymer melt affects polymer parison integrity. If the balance of properties is in favor of viscosity over elasticity, the polymer melt will not have good stability and tend to sag during certain extrusion processes. There is a strong correlation between extrudate swell ratios and parison integrity. The introduction of long chain branching in accordance with the present invention results in polymer melts having swell ratios indicative of good elastic properties for extrusion processes.

The presence of a small amount of long chain branching in a linear molecule increases elasticity of the polymer melt by introducing very long relaxation times in the relaxation spectrum of the melt. Since the polymer melt is a collection of molecules with different lengths and different branches, each molecule will respond differently to a given deformation. The collection of response times is referred to as the relaxation time spectrum which directly relates to the stability of the polymer melt during extrusion.

Long chain branching in accordance with the present invention has another important advantage of changing the elongational characteristics of polymer

melts. The presence of long chain branching increases the value of the longational viscosity and introduces a maximum elongation viscosity as a function of strain rate.

5 The polymers produced in accordance with the present invention have still another advantage of having a reduced tendency to melt fracture at high shear rates. Smooth extrudates of polymer melts may be obtained easily at low shear rates. However, above a  
10 critical shear rate, the extrudate becomes uneven. The form of distortion of the extrudate varies. In some cases, the extrudate has the form of a screw thread, in others, the extrudate becomes spiral twisted while in others the distortion may take on the affect of a  
15 regular ripple or even random distortions. The critical shear rate of a polymer is related to the degree of entanglement of the polymer. The greater the degree of entanglement of the polymer, the lower the critical shear rate. Since the polymers produced in  
20 accordance with the present invention, due to the linear long chain branching, have less entanglement than linear polymers, the critical shear rate of these polymers will be increased. The result is that polymers made in accordance with the present invention  
25 have a reduced tendency to melt fracture at high shear rates than conventional linear polymers.

The polymers of the present invention also enjoy the good solid polymer mechanical properties associated with short chain branching distributions of single site catalyst polymerizations. The polymers produced in accordance with the present invention may have high molecular weights with narrow molecular weight distributions. These narrow distributions result in products having lower extractables caused by amorphous  
30 waxes, better clarity due to the absence of large light  
35 refracting crystals, and superior impact resistant due

to increased number of tie molecules binding crystal regions together.

5 The frequency of chain branching is determined by <sup>13</sup>C NMR spectrometry for homopolymers and by measuring the viscous energy of activation of copolymers with a parallel plate oscillating shear melt rheometer.

10 Long chain branching may be detected by comparing the results of different gel permeation chromatography (GPC), measured with both a refractive index detector and a low angle laser light scattering detector. GPC separations are governed by the hydrodynamic volume of polymeric molecules in solution. The standard detector on most GPCs measures the relative refractive index (RI) of the effluent. The RI detector assumes that 15 molecules coming off the separation column at Time 1 have the same molecular weight as molecules eluting from an unbranched calibration standard at Time 1. It has been discovered that long chain branches do not increase the hydrodynamic volume of a molecule by an 20 amount proportional to the length of its branches. It is believed that the contribution in the hydrodynamic volume is only a fraction of the branch length. In other words, refractive index detectors cannot "see" 25 linear long chain branches in accordance with the present invention. However, a low angle light scattering (LALLS) detector does "see" all carbons in a polymer molecule. By analyzing a sample with both detectors, the difference in the results provides evidence of long chain branching in accordance with the 30 present invention. This technique is illustrated by the following data:

	Sample	Mw	Mw
		(DRI detector)	(LALLS detector)
35	A	99800	99900
	B	111000	116000
	C	206000	231000

Sample A is an ethylene-hexene copolymer made in a gas phase process with a metallocene catalyst which is known to have no long chain branches. By comparing the molecular weight values calculated by the standard refractive index detector (RI) and the LALLS detection method, one sees that there is no significant difference in the values suggesting there are no hidden branches. Comparing the RI and LALLS values for sample B, an increase of 5,000 in molecular weight is seen by the LALLS detection method. With sample C, a 25,000 molecular weight increase is detected. The higher molecular weight of samples B and C as determined with the LALLS detector are evidence of long chain branching.

By comparing the different GPC techniques for polymers in accordance with the present invention, one generally sees that molecular weight as calculated by the LALLS technique is greater than the molecular weight as calculated by the RI GPC technique.

Long-chain branching in polyethylene is defined as those branches which produce one or more of the following effects.

1. High viscous energy of activation (Ea).

Polymer viscous energy of activation can be determined with parallel plate shear melt rheometry. Melt viscosity-temperature dependence is determined by performing shear rate superposition. The resulting shift factors are fitted to an Arrhenius equation; the product is the viscous energy of activation.

The energies of activation for a variety of polyethylene types are illustrated in the bar chart of figure 1. HDPE represents narrow MWD, linear homopolymers in the 5-50 MI range. LLDPE represents narrow MWD, linear ethylene-butene copolymers with comonomer content ~12% and MI in the 1-2 dg/min range. HMW-HDPE represents narrow MWD, linear ethylene

homopolymers with  $M_w$ 's greater than 200k (i.e., MI < 0.2 dg/min). LDPE represents long-chain branched, ethylene homopolymers produced in a free-radical process. The LPE w/ LCB represents some of the branched polymers of this invention.

5 The unusually high  $E_a$  of the LPE w/ LCB is clear evidence of long-chain branching.

10 2. Low viscosity, moderate shear rates relative to unbranched NMWD linear polymers.

Melt viscosities can be measured vs. shear rate with a capillary rheometer. Figure 2 is an illustration of the relationship between the  $M_w$  of NMWD linear polyethylenes, and their melt viscosity measured at 15  $340\text{ s}^{-1}$  and  $190^\circ\text{C}$ . This data is narrowly distributed about a linear model: viscosity =  $0.0115 \times M_w - 325$ . The position of the LDPE samples reflects the known fact that LDPEs are more "shear thinning" than linear polyethylenes, i.e., their viscosities decrease more 20 rapidly as shear rate increases than do the viscosities of linear polyethylenes. The position of the LPE w/ LCB is clear evidence that this NMWD linear homopolymer contains long-chain branching. The branched polymers of this invention have a viscosity measured at 340sec- 25  $1/190^\circ\text{C}$  of  $0.75(0.0115 \times M_w - 325)$ .

3. High melt strength.

Melt strength can be determined with a Rheotens Instrument which consists of a capillary rheometer 30 equipped with an accelerating wheel take-off station. The melt tensile force in the capillary rheometer extrudate is measured as a function of the instantaneous wheel velocity. Figure 3 illustrates the relationship between melt tension, measured at  $190^\circ\text{C}$  35 immediately before the onset of severe draw resonance, and  $M_w$  for numerous unbranched, narrow MWD linear ethylene-alpha-olefin copolymers. These tensile forces

are narrowly distributed about a linear model: melt tensile force =  $(7.68 \times 10^{-5}) \times M_w - 4.32$ . The branched polymers of this invention will exhibit a melt tensile force of  $1.3((7.68 \times 10^{-5}) \times (M_w \text{ of the polymer}) - 4.32)$ .

The unusually high tensile force observed with the LDPE is attributed to its long-chain branching. Evidence of the maximum frequency of the long-chain branches in a linear polymer can be determined with carbon-13 NMR if the polymer contains no short-chain branches, due to the comonomer, which are larger than 3 carbons in length. The carbon atom in the polymer's backbone to which a branch, which is larger than 3 carbons in length, is attached produces a signal in the C13-NMR spectrum at 38 ppm, which is distinguishable from all other carbons in the qualifying test sample and therefore a measure of the maximum number of long-chain branch points.

The present invention may be illustrated by the following examples:

#### EXAMPLE 1 Macromer A

A one liter autoclave solution polymerization reactor was charged with 400 ml toluene, 40 psig ethylene, and 58.9mg  $Cp_2ZrMe_2$  & 11mg  $B(pfp)_3$  [Bis(cyclopentadienyl)Zirconiumdimethyl & tris (pentafluorophenyl) Boron)]. The mixture was reacted at 90°C (16° exotherm) for 0.87 hours. The polymerization yielded 121.4 grams of polymer after drying in a vacuum oven for 24 hours until odor-free. The dried polymer consisted of irregularly-shaped particles ranging in size from less than 0.1 mm to greater than 1 cm. The density of the polymer was  $0.953 \text{ g/cm}^3$ , with a weight-average molecular weight ( $M_w$ ) of 29,000 with a level of vinyl that was not detected by NMR, and an index of polydispersity ( $M_w/M_n$ ) of 3.28. The polymer had a chain branching frequency of 0.48 branches per 1,000

carbon atoms of the main polymer chains by  $^{13}\text{C}$  NMR analysis.

**EXAMPLE 2 Polymerization with Macromer A**

5       A one liter solution polymerization autoclave reactor was charged with 400ml toluene, 25g of macromer A produced in example 1 (linear ethylene homopolymer having a weight-average molecular weight ( $M_w$ ) of 29,000 with very low levels, i.e. not detected, of vinyl unsaturations per 1,000 carbon atoms) and 100 psig 10 ethylene, and 0.24 millimoles of bis (cyclopentadiene) dimethyl zirconium tris (pentafluorophenyl) boron catalyst (in toluene) with an initial reactor temperature of 45°C. The solution temperature was 15 raised to 102°C and reacted for 0.33 hours. The polymerization yielded 57.0 g of polymer after drying in a vacuum oven for 24 hours until odor-free. The dried polymer consisted of irregularly-shaped particles ranging in size from less than 0.1 mm to greater than 20 1.0 cm. The density of the polymer was 0.953 g/cm<sup>3</sup>, with a weight-average molecular weight ( $M_w$ ) of 82,500 and an index of polydispersity ( $M_w/M_n$ ) of 5.3. The polymer had a long chain branching frequency of 2 long chain branches per 1,000 main chain carbon atoms by  $^{13}\text{C}$  25 NMR analysis.

**EXAMPLE 3 Macromer B**

30       A one liter autoclave solution polymerization reactor was charged with 400 ml of hexane, 20 psig ethylene, and 60 mg of bis (cyclopentadiene) dimethyl zirconium catalyst and 60 mg of tris (pentafluoronyl) boron catalyst activator. The mixture was reacted at 90°C for 0.7 hours. The polymerization yielded 26g of 35 polymer after drying in a vacuum oven for 24 hours until odor-free. The weight-average molecular weight ( $M_w$ ) of the polymer was 21,000 and the index of polydispersity ( $M_w/M_n$ ) was 8.2. The polymer had a

chain branching frequency of 1.22 branches per 1,000 main chain carbon atoms of the main polymer chains by  $^{13}\text{C}$  NMR analysis.

5    **EXAMPLE 4 Polymerization with Macromer B**

A one liter autoclave solution polymerization reactor was charged with 400ml of toluene, 25g macromer B produced in example 3 (linear ethylene homopolymer having a weight-average molecular weight ( $M_w$ ) of 21,000 and 1.0 vinyl unsaturations per 1,000 carbon atoms) and 10 50 psig ethylene, and 0.24 millimoles bis (cyclopentadiene) dimethyl zirconium tris (pentafluorophenyl) boron catalyst (in toluene). The mixture was reacted at 60°C (42° exotherm) for 0.28 15 hours. The polymerization yielded 78.8g of polymer after drying in a vacuum oven for 24 hours until odor-free. The weight-average molecular weight ( $M_w$ ) was 32,000 and index of polydispersity or MWD, ( $M_w/M_n$ ) was 3.0. The polymer had a linear long chain branching 20 frequency of 0.48 branches per 1,000 carbon atoms of the main polymer chains by  $^{13}\text{C}$  NMR analysis.

CLAIMS

What is claimed is:

1. A branched polyolefin comprising:

5 a main chain (b) of a homopolymer or a copolymer of C<sub>2</sub> - C<sub>30</sub> alpha olefins; and side chains (a) of at least 250 carbon atoms comprising a homopolymer or a copolymer of C<sub>2</sub> - C<sub>30</sub> alpha olefins, said side chains being distributed along the polymer main chain at an 10 average frequency of 0.1 to 5 side chains per 1000 main chain carbon atoms, said branched polymer having a weight average molecular weight of at least 30,000 and an M<sub>w</sub>/M<sub>n</sub> of 6 or less.

15

2. The branched polyolefin of claim 1 wherein the side chains(a) are 300 to 3000 carbons long.

20

3. The branched polyolefin of claim 1 or 2 having a M<sub>w</sub> of 30,000 to 1,000,000.

4. The branched polyolefin of any previous claim having a M<sub>w</sub>/M<sub>n</sub> between 1 and 4.

25

5. The branched polyolefin of any previous claim having side chains(a) present at an average frequency of 0.2 to 3 side chains per 1000 main chain carbons.

30

6. The polyolefin of any previous claim wherein the side chains (a) derive from ethylene and any C<sub>3</sub> to C<sub>30</sub> alpha olefin and the main chain, independently, derives from ethylene and any C<sub>3</sub> to C<sub>30</sub> alpha olefin.

35

7. The branched polymer of any previous claim characterized by a density of 0.85 to 0.95g/cm<sup>3</sup>.

8. The branched polymer of any previous claim wherein the side chains (a) comprise block copolymer of ethylene and propylene.
- 5 9. The polymer of any previous claim wherein the side chains (a) comprise a polymer of any C<sub>3</sub> to C<sub>30</sub> alpha olefin with an ethylene block present at the insertion point along the main chain.
- 10 10. A polymer blend composition comprising at least 5 weight percent, based upon the weight of the composition, of a branched polyolefin of any previous claim.
- 15 11. A film or article of manufacture comprising the branched polymer of any previous claim.
12. A method for producing polyolefins of claims 1-10 comprising the steps of:
  - 20 1) contacting under polymerization conditions : one or more alpha olefin monomers with a catalyst system to produce a vinyl terminated macromonomer of at least 250 carbon atoms long;
  - 25 2) subsequently contacting, under polymerization conditions : said vinyl terminated macromonomer; with one or more alpha olefin monomers; and a catalyst system comprising a cyclopentadienyl transition metal catalyst and a cocatalyst or activator.
- 30 13. The method of claim 12, wherein the transition metal is Zr, Hf, or Ti.

14. The method of claims 12 or 13, wherein the cocatalyst activator is an alumoxane or a Lewis acid activator.
- 5 15. The method of claims 12, 13, or 14 wherein the polymerization conditions for step 2) are solution, gas phase, bulk phase, or supercritical phase polymerization conditions.
- 10 16. A branched polyolefin of claim 1 having energy of activation greater than about 9 kcal/mole or a viscosity of  $0.75 \times (0.0115 \times M_w \text{ of the polymer} - 325)$  and a melt strength  $1.3 \times (7.68 \times 10^{-5}) \times M_w - 4.32$ .
- 15 17. The method of claims 12 - 15, wherein the cyclopentadienyl transition metal catalyst is a transition metal compound comprising a single cyclopentadienyl group and a heteroatom containing group each bonded to the transition metal, said
- 20 20 cyclopentadienyl group and heteroatom containing groups optionally bridged through a divalent moiety.

## INTERNATIONAL SEARCH REPORT

Int. Application No  
PCT/93/08833A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C08F299/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,91 17194 (EXXON CHEMICAL PATENTS) 14 November 1991 see page 9, line 20 - line 26 see page 12, line 1 - line 28	1
A	EP,A,0 366 411 (EXXON CHEMICAL PATENTS) 2 May 1990	1
A	WO,A,92 00333 (EXXON CHEMICAL PATENTS) 9 January 1992 cited in the application	1,12
A	EP,A,0 129 313 (EXXON RESEARCH AND ENGINEERING) 27 December 1984 cited in the application & US,A,4 500 648	1
	-/-	

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*&\* document member of the same patent family

2

Date of the actual completion of the international search  29 December 1993	Date of mailing of the international search report  03.01.94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patenttaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  Andriollo, G

## INTERNATIONAL SEARCH REPORT

Int'l. Application No.  
PCT/3/08833

## C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LU,A,68 147 (AQUITAINE TOTAL ORGANICO) 16 October 1973 -----	1
2		

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Appl. No.  
PCT/EP/08833

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9117194	14-11-91	AU-A-	7875791	27-11-91
EP-A-0366411	02-05-90	AU-A- CA-A- JP-A-	4384289 2001462 3028209	03-05-90 28-04-90 06-02-91
WO-A-9200333	09-01-92	EP-A-	0551277	21-07-93
EP-A-0129313	27-12-84	US-A- AU-A- CA-A- JP-A- US-A- US-A-	4500648 2720184 1225096 60090203 4581467 4851489	19-02-85 01-11-84 04-08-87 21-05-85 08-04-86 25-07-89
US-A-4500648	19-02-85	AU-A- CA-A- EP-A, B JP-A- US-A- US-A-	2720184 1225096 0129313 60090203 4581467 4851489	01-11-84 04-08-87 27-12-84 21-05-85 08-04-86 25-07-89
LU-A-68147	16-10-73	FR-A- AU-B- AU-A- BE-A- CA-A- CH-A- CH-A- DE-A- GB-A- JP-A- NL-A- SE-A- US-A-	2198490 466644 5893673 803179 1011498 591529 591526 2339508 1429806 49132186 7310850 7702394 3887650	29-03-74 06-11-75 06-02-75 03-12-73 31-05-77 30-09-77 30-09-77 14-02-74 31-03-76 18-12-74 06-02-74 03-03-77 03-06-75